

# Evaluation of the quantitative analysis of PBDEs in plastics by thermal desorption GC-MS for soluble polymers

Franky Puype<sup>1</sup> and Jiří Samsonek<sup>1</sup>

<sup>1</sup>Institute for Testing and Certification, Trida T. Bati 299, CZ-764 21 Zlín, Czech Republic

## Introduction

The plastic waste stream from electric and electronic equipment (WEEE) might contain polybrominated diphenyl ethers (PBDEs) and polybrominated biphenyls (PBBs). To prevent further re-use and production of WEEE containing PBDEs and PBBs the European Union published a new regulation on 13 February 2003. This contains a restriction of hazardous substances (RoHS) like lead, mercury, cadmium, chromium (VI), PBBs and PBDEs. The RoHS became a law since July 2006. The content of these classes of persistent organic compounds in new electric and electronic equipment shall not exceed a limit of 1000 mg/kg<sup>1,2</sup>.

Various analytical methods for the quantification of PBDEs in plastics are based on a solvent extraction followed by GC-MS or LC-MS analysis. A fast alternative method is thermal desorption GC-MS (TD-GC-MS) analysis for the identification of the brominated flame retardants (BFRs). Optimisation has been done to quantify PBDEs in soluble plastics only by TD-GC-MS. Polycarbonate (PC), vinylpolymers like polystyrene (PS), polymethylacrylate (PMA) and copolymer acrylonitrile butadiene styrene (ABS) are polymers which easily solve in an organic solvent<sup>3,4</sup>. A film method based on solving the PBDE containing polymer is applied. The solution is spiked into the sample cup following by solvent evaporation at room temperature. A remaining thin polymer film is thermally desorbed and PBDEs are quantified by external calibration.

## Material and Methods

### Chemicals

All PBDE solutions used in this study are made from laboratory made technical mixtures of PBDEs in toluene (HPLC grade). The calibration PBDE mixtures of individual congeners were synthesised by AccuStandard (New Haven, CT, USA).

### Reference samples

The plastic materials were solved in solvents like toluene (PS, ABS), acetone (PMA) and dichloromethane (PC). The solutions were spiked with a known amount of PBDEs solved in toluene. The mixture was shaken for a long time till a homogeneous solution was reached. This solution was put on an aluminium foil and dried over night. This whole process is kept away from direct sunlight to avoid photodegradation of the PBDEs. A PBDE doped polymer film remains.

### Sample preparation - film method

The PBDE containing sample is solved in a HPLC grade solvent depending on the type of plastic and shaken. A few microliter of this PBDE/polymer solution was placed in a sample cup and dried. A thin polymer film remains in the cup and is measured by TD-GC-MS. The amount of thermal desorbed polymer is about 3 mg.

### TD-GC-MS method

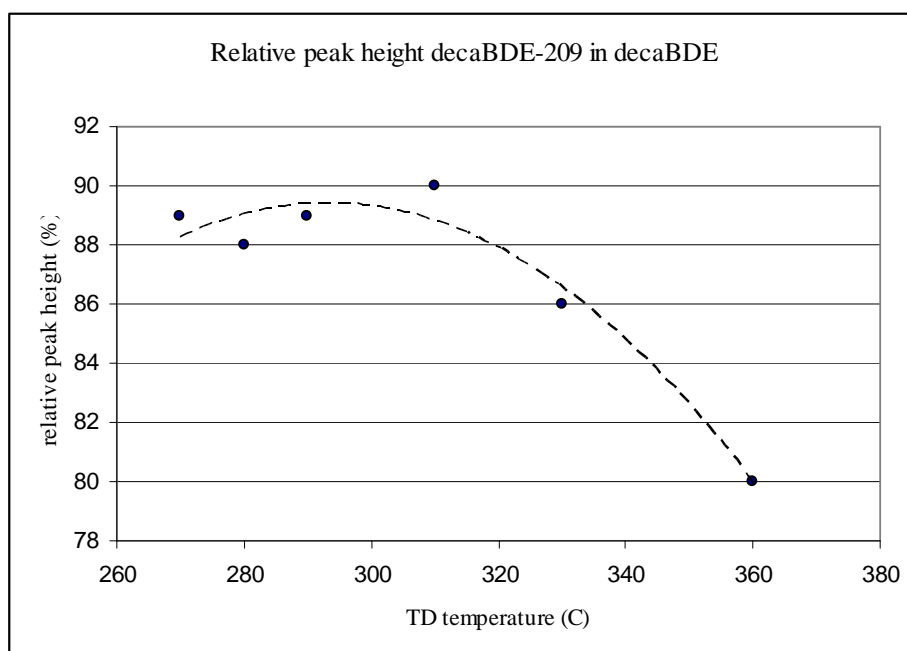
All experiments were carried out with a thermal desorption and pyrolysis unit PY-2020iD (Frontier Laboratories Ltd., Japan) with a 48 position auto sampler connected to a GC-MS-QP2010plus (Shimadzu, Japan). DecaBDE is a thermal labile product and requires a short residence time on the analytical column. Therefore a special metal capillary separation column (Ultra ALLOY-PBDE; 0.25 mm i.d. x 15 m, Frontier Laboratories Ltd., Japan)

coated with a very thin (0,05  $\mu\text{m}$ ) film of immobilized-polydimethylsiloxane is used. After optimising the desorption settings a thermal desorption temperature of 270°C for 10 minutes gave the highest and stable peak performance for decaBDE. The peaks are monitored in the FASST-mode (Fast Automated Scan/SIM Technique) which enables to acquire both Scan and SIM data on one peak. The quantification is done by external calibration. The congeners triBDE-28, tetraBDE-47, pentaBDE-99 and pentaBDE-100, hexaBDE-153 and hexaBDE-154, heptaBDE-183, octaBDE-203, nonaBDE-207 and decaBDE-209 are used for calibration. With these calibrations each PBDE homologue can be quantified.

## Results and Discussion

### *Optimisation of the thermal desorption parameters*

The optimisation of the thermal desorption temperature has been done with a technical mixture of decaBDE. DecaBDE-209 is thermally unstable and its peak height in technical decaBDE (Figure 1) has been relatively compared to the peak heights of the formed nonaBDE triplet and octaBDEs. Different thermal desorption temperatures were used (270°C-360°C for 4 minutes) with a similar interface temperature between the thermal desorption unit and the gas chromatograph.

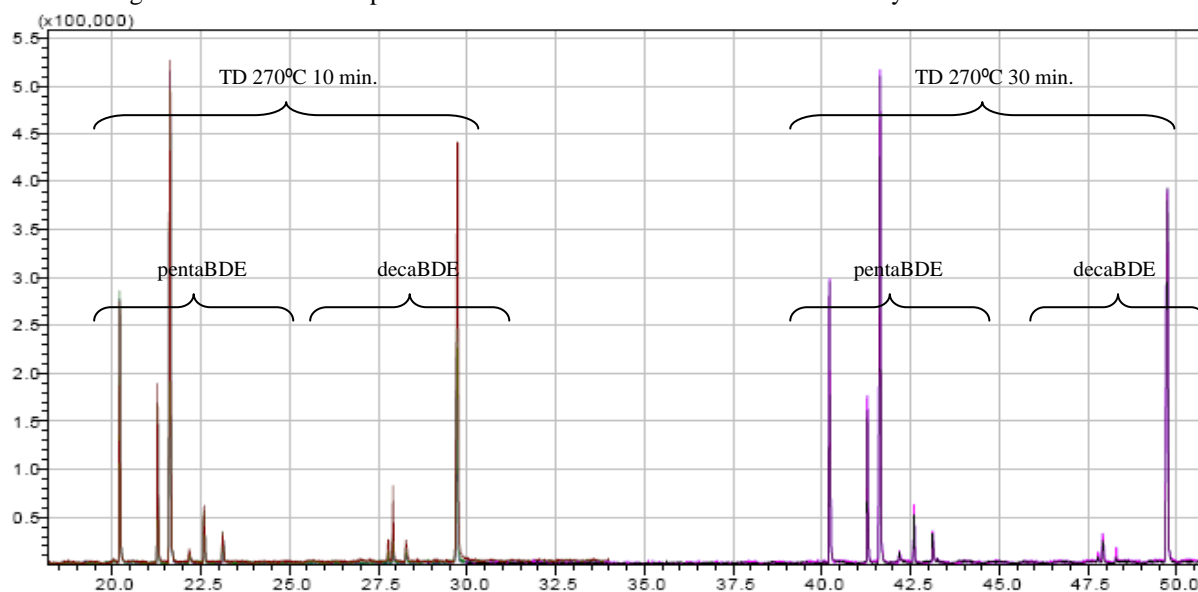


**Figure 1: Relative peak height of decaBDE-209 in technical decaBDE at different thermal desorption temperatures.**

The thermal desorption temperature has been chosen at 270°C because the thermal desorption temperature needs to be as low as possible. Thermal desorption temperatures higher than 300°C induce a critical debromination of the analyte.

The thermal desorption time has been defined by measuring technical pentaBDE and decaBDE at 270°C for 10, 15, 20 and 30 minutes. So far a thermal desorption time of maximum 4 minutes has been used but this time could not give sufficient reproducibility. The analyte needs more time to migrate completely from the polymer matrix. The results of the experiment are shown in Figure 2 where the peaks between  $t_R$  20 and 30 are the pentaBDE/decaBDE with 10 minutes thermal desorption. The peaks between  $t_R$  40 and 50 are the pentaBDE/decaBDE with 30 minutes thermal desorption. The peak areas for all thermal desorption times

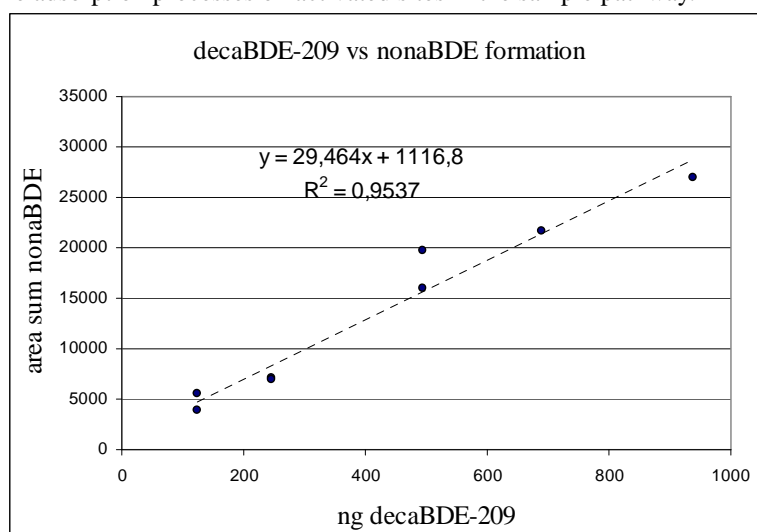
between 10 and 30 minutes are the same and a triple analysis gives a reproducibility between 3-20 % (RSD, n=3) for each congener. A thermal desorption time of 10 minutes is sufficient for the analysis.



**Figure 2: Overlay chromatogram of pentaBDE and decaBDE for a thermal desorption time of 10 minutes and 30 minutes.**

#### *Linearity and method range*

A linear relationship is evaluated across the range of the analytical procedure starting from 10 mg/kg individual PBDE congener. However decaBDE-209 congener shows at the beginning of the calibration curve an exponential tendency due to adsorption and break down. The break down of the decaBDE-209 congener is in thermal desorption a common process due to adsorption on residual char in the injector followed by debromination. Therefore the whole injector and thermal desorption furnace need to be cleaned/replaced before each sequence. Experiments prove that the nonaBDE formation happens in linear relationship with the amount of thermal desorbed decaBDE-209 (Figure 3). The exponential calibration of decaBDE-209 is mainly the responsibility from the adsorption processes on activated sites in the sample pathway.



**Figure 3: Relation between the decaBDE-209 concentration and the formed nonaBDEs**

### ***Recovery-Reproducibility***

The recovery of the analysis has been tested by the measurement of spiked polystyrene samples containing 1000 mg/kg pentaBDE and octaBDE. Recoveries between 106 and 123 % have been reached. The reproducibility for multiple analysis was ranging from 3 till 15 % (RSD, n=4) for each individual PBDE homologueous.

### ***Sensitivity-limits of detection***

The method is designed to quantify the individual PBDE congener at a level of 10 mg/kg for triBDE till heptaBDE and 30 mg/kg for octaBDE till decaBDE. The PBDE concentrations used are in a range of 160 mg/kg till 2000 mg/kg.

### ***Applicable for other BFRs***

So far the method is applicable for other BFRs like PBBs, tetrabromobisphenol A, decabromodiphenylethane, hexabromocyclododecane and tetrabromobisphenol A bis (2,3-dibromopropyl ether). However we have to be aware that the thermal desorption settings for some analytes give formation of degradation products.

### **Conclusions**

The quantitative measurement of PBDEs in plastics by thermal desorption GC-MS seems to be applicable for soluble polymers. The thin film method gives high recoveries and good reproducibility. The limit of detection of the method gives 160 mg/kg for the total PBDE content. DecaBDE-209 shows always a bit thermal degradation but can be minimised by working with a cleaned injector before each sequense.

The method might be called universal for BFRs because other common non-ROHS banned BFRs are also traceable in plastics. Further research will go on for PBBs in soluble polymers and not soluble polymers.

### **Acknowledgements**

This project was supported by the Ministry of Industry and Trade of Czech Republic. Tento projekt byl realizován za finanční podpory z prostředků státního rozpočtu prostřednictvím Ministerstva průmyslu a obchodu.

### **References**

1. BSEF, Bromine Science and Environmental Forum, <http://www.bsef.com>
2. Jakab E, Uddin Md. A, Bhaskar T, Sakata Y. *Journal analytical and applied pyrolysis*. 2003;69:83
3. Billmeyer F. *Textbook of polymer science*, 1984; 244-245.
4. Yuncheol N, Jungju S. *Bull.Korean Chem. Soc.*,2003;24/9;1276.